Experimental measurement of crystal-melt interfacial energy

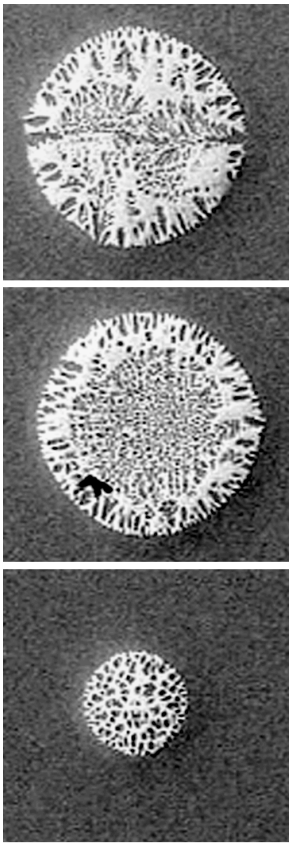
Wulff's description of the relationship between the interfacial free energy function, $\gamma(n)$, and the equilibrium shape of a droplet, $r(n)$, facilitates unique determination of $\gamma(n)$ from measurements of the equilibrium shape. In metallic systems, the magnitude of the anisotropy may be very low, but critical to the relative stability and selection of dynamic interface morphologies. For these low-anisotropy systems, the equilibrium shapes typically exhibit no missing orientations. At the same time, the low-amplitude variation of $\gamma(n)$ makes experimental measurement very challenging, since the equilibrium shape differs only slightly from that of a sphere.

The 3-D equilibrium shape may be considered in two dimensions by examining a particular cross-section, *{hkl}*, through the equilibrium shape, and the corresponding two-dimensional slice of the Wulff plot, can be expressed generally as

$$\frac{\gamma_q}{\gamma_0} = 1 + \sum_{m=2}^{k} \gamma_m^q \cos(m\theta)$$

where m is the degree of rotational crystal symmetry for each mode about the section plane normal, and $q=\langle hkl \rangle$ is the cross-section normal. For a cubic metal, it is often assumed that $\gamma(\theta)$ taken on a {100} plane, is dominated by the $m=4$ term, and all other terms are ignored. Thus the value of the anisotropy parameter, γ_4^{001}, can be estimated from experimental measurement of this equilibrium shape on selected 2-D sections.

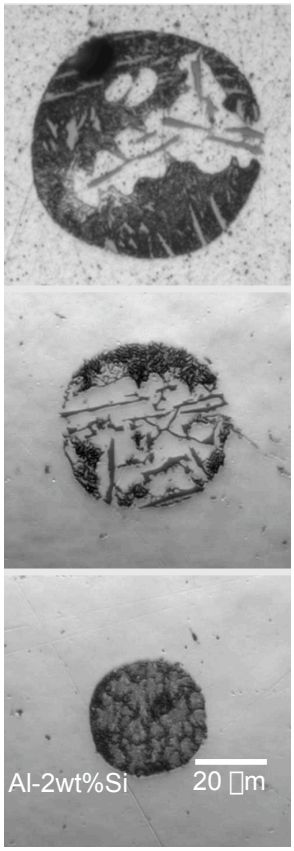
In this work, we utilize a heat treatment sequence that produces a low volume fraction dispersion of fine droplets entrained within a single-phase solid, away from any grain boundaries. The salient feature of our method is that it does not involve nucleation from a single-phase solid. Rather, the liquid droplets are formed through localized liquation at the phase boundaries which are remnant from a prior directional solidification process. Moreover, because the specimens are directionally solidified, all grains in the resulting coarse-grained specimen share a common <100> direction that is aligned with the specimen axis. Transverse sections of the specimen, therefore, are on {100} planes. Crystallographic orientation can be controlled further, by growing the specimen from a single-crystal seed that is aligned along a particular direction. This practice serves to avoid grain boundary droplets and provides a unique and predictable crystallographic orientation for the entire dispersion.



Equilibrium shape measurements were performed using Al-4wt%Cu and Al-2wt%Si alloys. Droplet shapes were examined on {100} planes using both optical and scanning electron microscopy, and typical quenched droplets are shown in the figure to the left. Observed droplet diameters ranged between 10 and 200 μm in the Al-Cu specimen and between 20 and 50 μm in the Al-Si specimen. X-ray microchemical analysis was used to verify that equilibrium conditions were obtained in the droplets and to quantify the effects of the quench. For each droplet measured, the pair of concentric circles that are multiply tangent to the droplet with the largest difference in diameters is first identified. These minimum and maximum diameters are offset by $\pi/4$, and the four-fold normalized anisotropy parameter is given by $\gamma_4=a_{001}/r_0=(\delta-1)/(\delta+1)$, where we define $\delta=d_{max}/d_{min}$.

A total of 28 droplets were measured in the Al-Cu sample. The associated anisotropy parameter exhibits a normal distribution with a mean value of γ_4=0.0097 and a 95% confidence interval of ±0.0008. A total of eight

droplets were measured in the Al-Si sample with a mean value of Γ_4=0.0169. These values represent the first quantitative measurements of interface energy anisotropy in metallic systems.



Significance:

The experimental measurements performed here are instrumental in the advancement of interface theory. The anisotropy of interfacial energy, while small in magnitude, plays a critical role in the selection of solidification morphology. As we begin to explore the origins of anisotropic properties and the influence on fundamental interface behavior using various atomistic descriptions, the independent measurement of physical properties becomes imperative for the development and verification of new theory.

Future Work:

Investigation of the effects of compostion is currently in progress for the Al-Cu and Al-Si binary systems. In addition, we aim to more generally determine the three-dimensional form of the Wulff plot, which will provide insight into several poorly understood selection behaviors observed in dendritic structures, and other characteristic dynamic growth morphologies.

Interactions:

Driven in part by theoretical investigations of interfacial behavior, this work is directly related to concurrent research being performed within the DOE-CMSN. In addition, many of the issues important in interface behavior are of mutual interest among the *Solidification Science* and the *Amorphous and Aperiodic Materials* focus areas within the Ames Laboratory Metal and Ceramic Sciences Program.